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SYNTHESIS AND SULFURATION OF 2'-ADAMANTYLIDENE-9-BENZONORBORNENYLIDENE†

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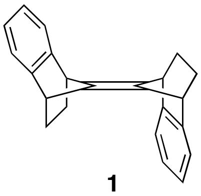
Abstract – A novel alkene, 2'-adamantylidene-9-benzonorbornene **6**, was synthesized from 2-adamantanone **7** in three steps resulting in a good overall yield. The alkene **6** reacted with elemental sulfur in refluxing *o*-$Cl_2C_6H_4$ to give *syn*-thiirane **14**, *anti*-thiirane **15**, and **6**. Almost the same ratio of the products was obtained when **14** or **15** was reacted with and without elemental sulfur under the same conditions. Sulfuration with Ph_3CSCl in CH_2Cl_2 at –78 °C afforded **14**, and that at room temperature furnished a 3:1 mixture of **14** and **15**. In contrast, although the sulfuration with Ph_3CSCl in CH_2Cl_2 at room temperature afforded **14** quantitatively, that at –78 °C gave **14** and **15** in 12 and 3% yields, respectively. Sulfuration by 1 molar equiv. of S_2Cl_2 or SCl_2 afforded **14** and *vic*-dichloride **28**.

INTRODUCTION

Considerable attention has been paid to the study of the sulfuration of alkenes because sulfuration is important as a model reaction of the vulcanization of rubber, and is it easy to introduce sulfur atoms into their C=C bonds.[1] One of the goals of its study would be the control of the number of sulfur atoms introduced. The number was found to noticeably depend on the structure of the alkenes when elemental sulfur was used as the sulfurating agent.[2−5] Although, in most cases, sulfuration gives a complex mixture containing polymeric compounds, cyclic oligosulfanes are obtained as the principal component in some cases. Thus, the sulfuration of norbornene and dibenzobarrelene by elemental sulfur gave a mixture of the corresponding 1,2,3-trithiolane and 1,2,3,4,5-pentathiepane,[2,3] and that of acenaphtho[1,2-*a*]-acenaphtylene afforded the corresponding pantathiepane as a sole product.[4] On the other hand, sterically congested 2,2'-biadamantylidene reacted with elemental sulfur to furnish the corresponding thiirane exclusively.[3] Sulfurations of *anti*- and *syn*-9,9'-bibenzonorbornenylidenes, **1** and **2**,[6] by elemental sulfur afforded the corresponding thiiranes, **3** and **4**, respectively, with retention of the original stereochemistry, whereas those by S_2Cl_2 afforded a mixture of **3**, **4**, and *vic*-dichloride **5**.[5] We have been interested in introducing one sulfur atom into alkenes, that is, directly synthesizing thiiranes from alkenes. Although some number of direct syntheses has been reported so far, most of the methods seem to be specific to the starting alkenes and present difficulties in synthesizing sulfurating agents.[7] Furthermore, most alkenes used in the study were hard to handle in laboratories, because the separation and analysis of the reaction mixture were difficult to achieve. We have designed a model alkene suitable for investigation into the reaction conditions for direct synthesis because of its ease in handling. Using **1** and **2** in the study would facilitate the analysis of the reaction mixture by ^{1}H NMR and, therefore, **1** and **2** were thought to be a good candidate for the alkene. However, their synthesis from a commercial compound is lengthy and an extra reaction step is required in order to separate the two alkenes.[6] We have designed a novel alkene carrying a 9-benzonorbornenylidene group to overcome the faults of **1** and **2**. Here, we report the synthesis of 2'-adamantylidene-9-benzonorbornenylidene and its sulfuration.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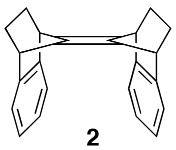
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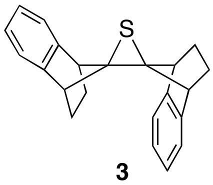

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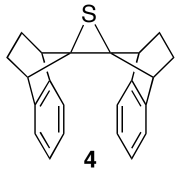

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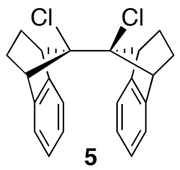

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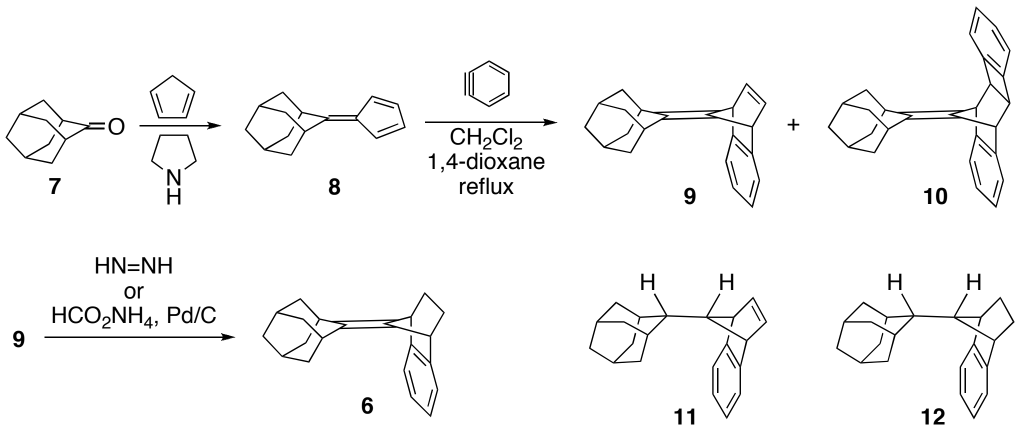
RESULTS AND DISCUSSION

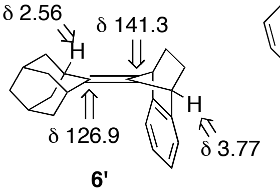
Synthesis of 2'-Adamantylidene-9-benzonorbornene 6

2’-Adamantylidene-9-benzonorbornenylidene **6** was synthesized from commercially available 2-adamantanone **7** in three steps. The ketone **7** was treated with cyclopentadiene in the presence of pyrrolidine to give fulvene **8**.[8] Reaction of **8** with benzyne, generated by reaction of anthranilic acid with isoamyl nitrite in CH_2Cl_2 and dioxane at reflux, afforded diene **9** in 96% yield together with bis-adduct **10** in 3% yield. The diene **9** was hydrogenated with HN=NH, generated by oxidation of H_2NNH_2 with $NaIO_4$, occurred chemoselectively to give **6** as colorless crystals in 98% yield.[9] Hydrogenation with HCO_2NH_4 in

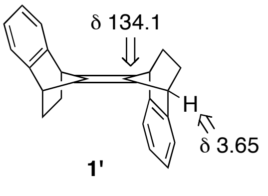


the presence of 5% Pd/C in MeOH/$CHCl_3$ (1:1) at reflux also afforded **6** in 87% yield.[10] Neither **11** nor **12** was obtained in either reaction.

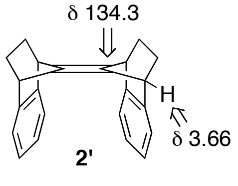
The alkene **6** showed five multiplets centered at δ 1.21 (2H), 1.76 (14H), 3.77 (2H), 7.04 (2H), and 7.14 (2H) and one broad singlet at δ 2.56 (2H) in the ^1H NMR spectrum. The bridgehead hydrogen signal of the 2-benzonorbornenylidene group (δ 3.77) appeared at a lower field than the corresponding signals of **1** (δ 3.65) and **2** (δ 3.66),[6] whereas that of the 2-adamantylidene group (δ 2.56) appeared at a higher field than the corresponding signals of 2,2'-biadamantylidene **13** (δ 2.95).[11] The ^{13}C NMR spectrum showed a higher field shift of the sp^2 carbon signal of the 2-adamantylidene group (δ 126.9) and a lower field shift of the sp^2 carbon signal at the 9-position of the 9-benzonorbornenylidene group (δ 141.3) by comparison with the corresponding carbon signals of **1** (δ 134.1), **2** (δ 134.3), and **13** (δ 133.1). These sizable upfield or downfield shifts would be caused by the homoconjugation interaction between the central C=C bond and the benzene ring shown as **6"**.[12]



6'



1'



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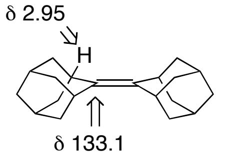

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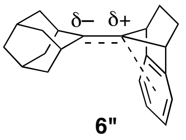
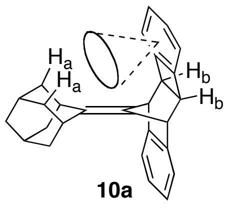
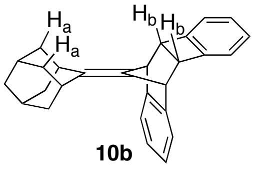


6"



10a

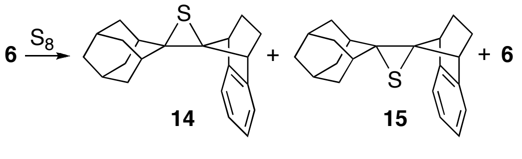


10b

The bis-adduct **10** was a product by cycloaddition reaction of **9** and benzyne.[13] The structure of **10** was *exo*- or *endo*-adduct, **10a** or **10b**, with respect to the benzene ring of **9**. Since no single crystals of **10** suitable for an X-ray analysis were obtained, the ^1H NMR spectrum of **10** was compared with the spectra of **10a** and **10b** calculated by Gaussian 98.[14] Thus, **10** showed five multiplets centered at δ 0.75 (2H), 1.59 (10H), 3.24 (2H), 3.86 (2H), and 7.12 (8H) and one broad singlet at δ 2.39 (2H) in the ^1H NMR spectrum. The multiplet centered at δ 0.75, assigned to axial hydrogens (H_a) at the 4-position of the adamantylidene group, appeared at a higher field than the corresponding signals in **9** and **6**, and that centered at δ 3.24, assigned to hydrogens (H_b) on the cyclobutene ring, developed newly when the further benzene ring was introduced into **6**. The calculation of **10** at B3LYP/6-311+G(2d,p) level shows that the H_a and H_b signals appear at δ 0.96 and 3.13 for **10a** and at δ 1.86 and 3.74 for **10b**, respectively, revealing that the structure of **10** proves to be **10a**. The ring current effect of the close benzene ring would result in the higher field shift of the signal of H_a.

Sulfuration of 2'-Adamantylidene-9-benzonorbornene 6 by Elemental Sulfur

The alkene **6** was sulfurated with elemental sulfur (1 molar equiv. as S_8) in refluxing *o*-$Cl_2C_6H_4$ to furnish *anti*- and *syn*-thiirane, **14** and **15**, in 76 and 4% yields, respectively, together with **6** in 19% yield. The sulfuration in DMF at 135 °C afforded **14** and **15** in 54 and 6% yields, respectively, along with **6** in 40% yield. Prolonging the reaction time did not bring about the disappearance of **6** in spite of the presence of an excess of sulfur atoms. These observations suggest that sulfuration must be reversible.[15]

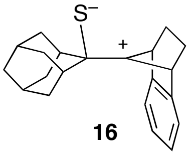


conditions	14	15	6
o-$Cl_2C_6H_4$, refl., 2 d	76%	4%	19%
DMF, 135 °C, 2 d	54%	6%	40%

Actually, **15** reacted with and without elemental sulfur in refluxing *o*-$Cl_2C_6H_4$ to afford about 19:1:5 and 23:1:9 mixtures of **14**, **15**, and **6**, respectively. The reactions of **14** gave almost same the product ratios as did that of **15**. The calculations for **14** and **15** at the B3LYP/6-311+G(2d,p) level predict that **14** is thermally more stable by 3.2 kcal mol^{-1} than is **15**.[14] The energy difference means that the calculated equilibrium ratio of **14** to **15** at 180 °C, the boiling point of *o*-$Cl_2C_6H_4$, is 32:1. The solvent effect would make the calculated ratio slightly higher than the actual ratios. Two mechanisms of the reversible process might be possible. One includes direct decomposition of the thiiranes to **6** and elemental sulfur, followed by the resulfuration of **6**. The other contains three consequent processes: 1) cleavage of the C—S bond close to the 9-benzonorbornenylidene group heterolytically or homolytically to give intermediates **16** and **17**, or **18** and **19**, 2) rotation about the central C—C bond, and 3) recombination of the C—S bond or elimination of sulfur from the intermediates.

$$\mathbf{14} \text{ or } \mathbf{15} \xrightarrow[\substack{o\text{-}Cl_2C_6H_4 \\ \text{refl., 2 d}}]{S_8} \mathbf{14} + \mathbf{15} + \mathbf{6} + S_8$$

substrate	molar equiv. as S_8	14	15	6
14	1	78%	4%	18%
14	none	70%	3%	27%
15	1	77%	4%	19%
15	none	69%	3%	28%



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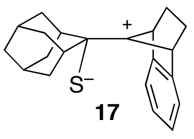

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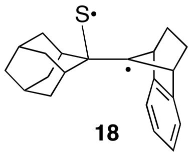

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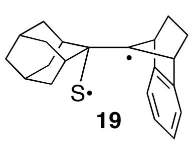

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Structure of 14 and 15

A molecular structure of **14** is shown in Figure 1. Selected bond length and bond angle data are summarized in Table 1. The C(2)—C(3) bond length, 1.477(2) Å, is slightly shorter than that of the parent thiirane, 1.484 Å,[16] and is slightly longer than those of **3** and **4**, 1.464(3) and 1.455(4) Å,[6] respectively. At the same time, the S(1)—C(2) bond length, 1.817(2) Å, is nearly equal to that of the parent thiirane, 1.815 Å, but the S(1)—C(3) bond length, 1.856(2) Å, is longer. The C(2)—S(1)—C(3) and S(1)—C(3)—C(2) bond angles, 47.39(7) and 64.89(9)°, respectively, are smaller than those of the parent thiirane, 48.16 and 65.52°,[16] respectively, but the S(1)—C(2)—C(3) bond angle, 67.72(9)° is larger. Deformation of the thiirane ring is probably due to steric repulsion among the S(1) atom and some hydrogen and carbon atoms in the substituents.

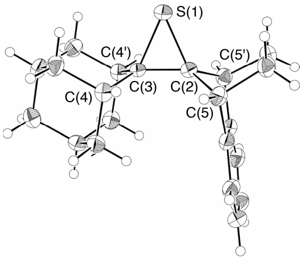
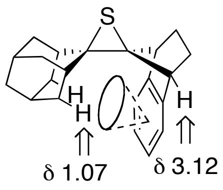


Figure 1. An ORTEP Drawing of **14**

Table. Bond Lengths and Bond Angles Data of **14**

Bond Lengths (Å)		Bond Angles (°)	
S(1)-C(2)	1.817(2)	C(2)-S(1)-C(3)	47.39(7)
S(1)-C(3)	1.856(2)	S(1)-C(2)-C(3)	67.72(9)
C(2)-C(3)	1.477(2)	S(1)-C(3)-C(2)	64.89(9)
C(2)-C(5)	1.544(2)	C(2)-C(3)-C(4)	121.16(8)
C(3)-C(4)	1.520(2)	C(3)-C(2)-C(5)	126.50(9)
		C(4)-C(3)-C(4')	110.87(13)
		C(5)-C(2)-C(5')	95.28(12)

In the ^{1}H NMR spectra, the two hydrogen atoms of the methylenes of **14**, which face the benzene ring and hence are placed under the influence of the ring current effect of the benzene ring,[6] appeared as a multiplet centered at δ 1.07, which is a higher field than the multiplet centered at δ 2.00 assigned to the corresponding methylene hydrogens of **15**. The bridgehead protons in the benzonorbornenylidene group of **14** and **15** appeared as a multiplet centered at δ 3.12 and 3.29, respectively, which are apart from the corresponding protons of **6** (δ 3.77), suggesting that, if a reaction mixture of the sulfuration of **6** contains only **14**, **15**, and **6** as compounds having protons that appeared in the range δ 3–4, a ratio of the mixture could easily be determined by ^{1}H NMR analysis.



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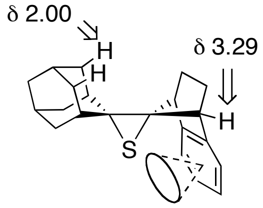


15'

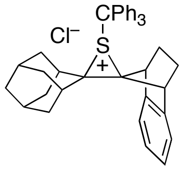
Sulfurations of 6 by Ph$_3$CSCl and Ph$_3$CSSCl

The alkene **6** reacted with 1 molar equiv. of Ph$_3$CSCl[17] in CH$_2$Cl$_2$ at –78 °C to give **14** in 60% yield along with **6** in 40% yield. A mixture of **14**, **15**, and **6** was obtained when the reactions were performed above –18 °C, and the ratio of **14** to **15** decreased as the reaction temperature increased. The yield of **6** increased

$$\mathbf{6} \xrightarrow[\text{CH}_2\text{Cl}_2\text{, 2 h}]{\text{Ph}_3\text{CSCl or Ph}_3\text{CSSCl}} \mathbf{14} + \mathbf{15} + \mathbf{6}$$

reagent	temp.	14	15	6
Ph$_3$CSCl	–78 °C	60%		40%
Ph$_3$CSCl	–18 °C	50%	10%	40%
Ph$_3$CSCl	RT	30%	10%	60%
Ph$_3$CSSCl	–78 °C	12%	3%	85%
Ph$_3$CSSCl	–18 °C	14%	3%	82%
Ph$_3$CSSCl	RT	quant.		

at rt because Ph_3CSCl decomposes into Ph_3CCl and elemental sulfur by the thiiranes prior to reacting with **6**.[5] In fact, Ph_3CSCl reacted with **14** in CH_2Cl_2 at rt to form Ph_3CCl, elemental sulfur, and **14** quantitatively. In contrast to these results, when **6** reacted with 1 molar equiv. of Ph_3CSSCl, the ratio of **14** to **15** increased as the reaction temperature increased. In particular, the reaction at rt furnished **14** exclusively. The possible mechanism of the sulfurations is as follows. The alkene **6** reacts with Ph_3CSCl to form thiiranium intermediates, **20** and **21**. The intermediates liberate triphenylmethylcarbenium ions, which react with chloride ions to give Ph_3CCl, *via* an E1 process to form the thiiranes.



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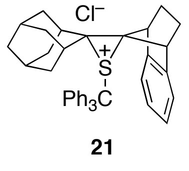

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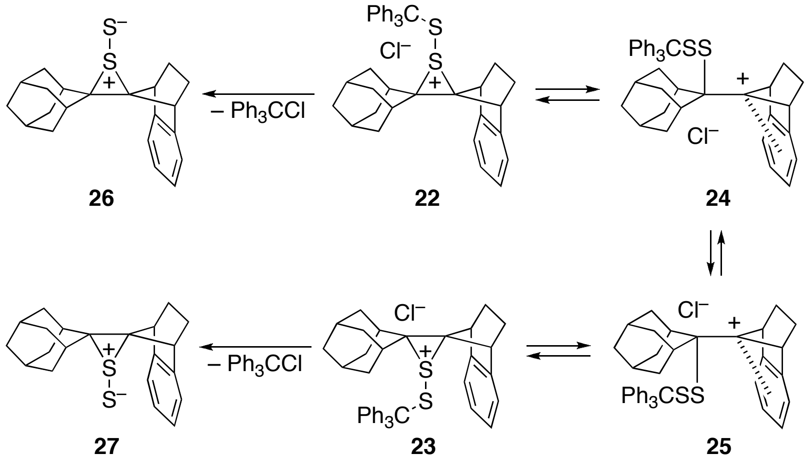
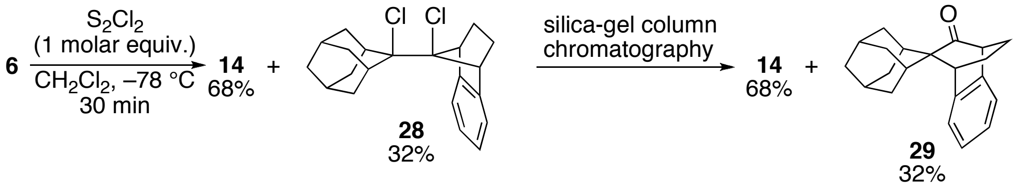
On the other hand, **6** reacts with Ph_3CSSCl to afford thiiranium intermediates, **22** and **23**. The intermediates have the less polar Ph_3C–S bond compared with **20** and **21**, hence the liberation of triphenylmethylcarbenium ion from **22** and **23**, which form thiirane sulfides, **26** and **27**,[18] and Ph_3CCl, becomes slower. The C—S bond of **22** and **23** that is close to their 9-benzonorbornenylidene group cleaves easily to form carbenium salts, **24** and **25**, which are stabilized by neighboring group participation of their benzene ring. Rotation about the central C—C bond of the carbenium salts, followed by recombination of the C—S bond takes place to furnish **26** and **27**.[19] The equilibrium among **22**—**25** in which **22** must be most stable, occurs under the reaction conditions. Finally, **26** and **27** eliminate sulfur to give **14** and **15**, respectively.

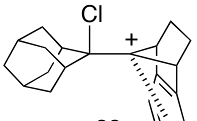


Sulfurations of 6 by S_2Cl_2 and SCl_2

The alkene **6** was sulfurated with 1 molar equiv. of S_2Cl_2 in CH_2Cl_2 at –78 °C. After the sulfuration was quenched by the addition of water at the same temperature, a 68:32 mixture of **14** and *vic*-dichloride **28** was obtained. Purification of the mixture by silica gel column chromatography furnished **14** and ketone

29 in 68 and 32% yields, respectively.[20] The ketone **29** is most likely formed by silica gel catalyzed hydrolysis of **28** to chlorohydrin **32** through formation of the carbenium ion **30**, which is in equilibrium with the epichloronium ion **31**, followed by pinacol-type rearrangement of **32**. The *vic*-dichloride **28** was not obtained from the reaction mixture in pure form. Therefore, **28** was synthesized separately by chlorine addition of **6** to confirm its structure. Reaction of **6** with 1.0 molar equiv. of SO_2Cl_2 in CH_2Cl_2 at –78 °C gave **28** whose spectral data were the same as those of the product that was formed by the sulfuration in quantitative yield.





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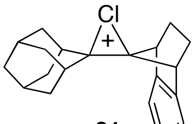

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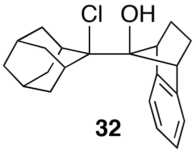

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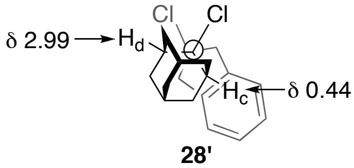


28'

Temperature-variable ^1H NMR spectra of **28** showed that all signals broaden at rt and separate sharply as the temperature falls. The signal (δ 0.44) due to the H_c atom at the 1-position of the adamantylidene group appeared at a higher field than that (δ 2.99) due to the H_d atom at the 3-position at –50 °C, revealing that **28** adopts a *gauche* conformation like **28’** at low temperatures.[21] Rotation about its central C—C bond occurs as the temperature gradually rises.

Sulfuration with 1.0 molar equiv. of SCl_2 furnished **14** and **28** in 42 and 57% yields, respectively. When **6** was sulfurated with 0.5 molar equiv. of S_2Cl_2 at –78 °C, **14** and **15** were obtained in 71% and 7% yields, respectively, revealing that two sulfur atoms of S_2Cl_2 are involved with the formation of thiiranes and, even if **15** is formed by the sulfuration, further reaction of **15** with S_2Cl_2 would occur to form **14** and **28**.

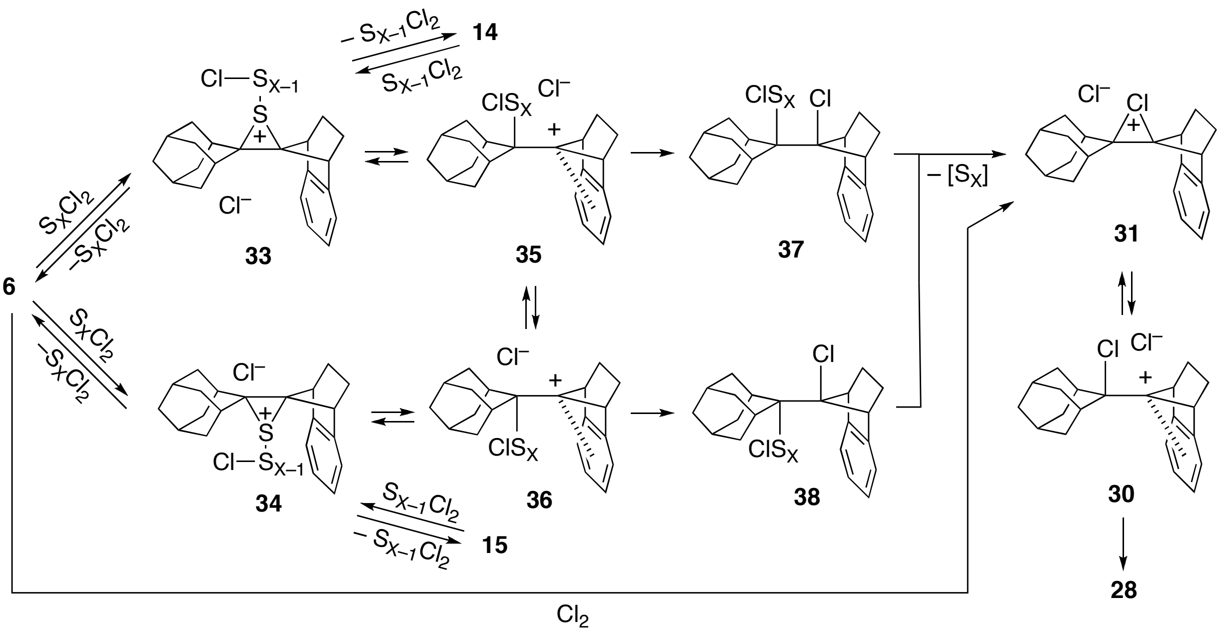
$$\underset{42\%}{\mathbf{14}} + \underset{57\%}{\mathbf{28}} \xleftarrow[\substack{CH_2Cl_2,\ -78\ ^\circ C \\ 30\ \text{min}}]{\substack{SCl_2 \\ (1\ \text{molar equiv.})}} \mathbf{6} \xrightarrow[\substack{CH_2Cl_2,\ -78\ ^\circ C \\ 30\ \text{min}}]{\substack{S_2Cl_2 \\ (0.5\ \text{molar equiv.})}} \underset{71\%}{\mathbf{14}} + \underset{7\%}{\mathbf{15}} + \underset{21\%}{\mathbf{28}}$$

In fact, **15** reacted with S_2Cl_2 under the same conditions as the sulfurations of **6** to afford **14** and **28** in 91% and 9% yields, respectively. The same reaction of **15** with SCl_2 and those of **14** with S_2Cl_2 and SCl_2 occurred to give a mixture of **14** and **28**.

$$\mathbf{15}\ \text{or}\ \mathbf{14} \xrightarrow[\substack{CH_2Cl_2,\ -78\ ^\circ C \\ 30\ \text{min}}]{\substack{S_XCl_2 \\ (1\ \text{molar equiv.})}} \mathbf{14} + \mathbf{28}$$

thiirane	X	**14**	**28**
15	2	91%	9%
15	1	66%	33%
14	2	78%	22%
14	1	58%	41%

The possible mechanism of the sulfuration with S_XCl_2 is as follows. The alkene **6** reacts with S_XCl_2 to form thiiranium salts, **33** and **34**. Then, **14** and **15** are produced from the salts together with SCl_2 (X = 2) or Cl_2 (X = 1). Cl_2 is also produced by equilibrium SCl_2 and S_2Cl_2,[22] and reacts with **6** to give **28**. After **33** and **34** come to equilibrium with the carbenium salts, **35** and **36**, isomerization of **15** to **14** and formation of the sulfanyl chlorides, **37** and **38**, proceed. The reason **14** is a main product having a sulfur atom seems to be its thermal stability compared with **15**. The epichloronium salt **31** is formed by elimination of sulfur from **37** and **38**, and then is finally transformed into **28**.



CONCLUSION

We succeeded in synthesizing a novel alkene **6** from commercially available 2-adamantanone in three steps. The sulfuration of **6** with elemental sulfur proceeded to give a mixture of thiiranes **14** and **15**. The *syn*-thiirane **15** was readily transformed into the alkene **6** and thermally more stable **14** under the sulfuration conditions, although no other products having sulfur atoms such as polymers and cyclic oligosulfanes were observed. The sulfuration with SCl_2 and S_2Cl_2 afforded **14** and *vic*-dichloride **28**. A ratio of the sulfuration products could easily be determined by their ^{1}H NMR spectra. From these results, we believe that **6** is a good candidate for the model alkene for studying the reaction conditions of the direct synthesis of thiiranes from alkenes, and have been using **6** to investigate the reaction conditions of direct synthesis with general applicability.

EXPERIMENTAL

Solvents were dried and purified in the usual manner. All the reactions were carried out under argon. Silica-gel column chromatography was performed on silica gel 60N (Kanto, 63—210 μm, spherical, neutral). Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker DRX400, a Bruker ARX400, a Bruker AM 400 (400.4 MHz for ^{1}H and 100.6 MHz for ^{13}C), a Bruker AC300P (300.1 MHz for for ^{1}H and 75.5 MHz for ^{13}C), or a Bruker AC200 (200.1 MHz for for ^{1}H and 50.3 MHz for ^{13}C) spectrometer using $CDCl_3$ or CD_2Cl_2 as the solvent with TMS for ^{1}H and with $CDCl_3$ or CD_2Cl_2 for ^{13}C as the internal standard. IR spactra were recorded on a Hitachi FT-IR 660+ spectrophotometer. Mass spectra were recorded on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode or using *m*-nitrobenzyl alcohol as a matrix in the FAB mode. Elemental analyses were performed by the molecular Analysis and Life Science Center of Saitama University.

Reaction of Fulvene 8 with Benzyne. To a solution of **8**[8] (4.0 g, 20 mmol) and isoamyl nitrite (4.1 mL, 30 mmol) in CH_2Cl_2 (160 mL) was added dropwise a solution of anthranilic acid (4.15 g, 30 mmol) in dioxane (40 mL) at reflux for 1 h. After the addition was finished, the reaction mixture was cooled to rt and then evaporated. Hexane and aqueous $NaHCO_3$ solution were added to the residue and then the insoluble materials were collected by filtration. After the filtrate was separated, the organic layer was washed with H_2O, dried over K_2CO_3, and evaporated. The residue was chromatographed on a column of silica gel and the column was eluted with hexane to give 5.3 g (96%) of **9** and 0.21 g (3%) of **10** in this order. 2'-Adamantylidene-9-benzonorbornadienylidene **9**: colorless crystals (from CH_2Cl_2 and hexane); mp 90—91 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 1.42—1.60 (m, 2H), 1.65—1.95 (m, 10H), 2.58 (br s, 2H), 4.30—4.40 (m, 2H), 6.80—7.00 (m, 4H), 7.11—7.28 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 28.3, 28.5, 32.7, 37.2, 38.3, 38.5, 49.7, 117.4, 120.5, 124.1, 143.2, 151.0, 155.3; IR (KBr) 3061, 3002, 2990, 2923, 2851, 1556, 1447, 784, 761, 749, 723, 693, 552, 447 cm^{-1}. Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.78; H, 8.23. 2'-Adamantylidene-9-(2,3-*o*-phenylenebenzonorbornadienylidene) **10**: colorless powder (from benzene); mp 295—298 °C; ^{1}H NMR (400.4 MHz, CD_2Cl_2) δ 0.69—0.77 (d-like, 2H), 1.43—1.57 (m, 5H), 1.60—1.68 (m, 4H), 1.72—1.77 (m, 1H), 2.38 (br s, 2H), 3.29 (s, 2H), 3.87 (s, 2H), 7.07—7.13 (m, 4H), 7.17—7.21 (m, 2H), 7.23—7.27 (m, 2H); ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 27.9, 28.3, 33.7, 37.2, 38.5, 38.8, 45.6, 49.5, 120.8, 122.2, 125.5, 127.3, 133.5, 136.3, 145.6, 147.4; IR (KBr) 3067, 2994, 2951, 2916, 2894, 2841, 1456, 1445, 767, 752, 743, 686, 678, 439 cm^{-1}. Anal. Calcd for $C_{27}H_{26}$: C, 92.52; H, 7.48. Found: C, 92.26; H, 7.52.

Reaction of 9 with Diimide. To a mixture of **9** (1.60 g, 5.8 mmol), $H_2NNH_2 \bullet H_2O$ (7.3 g, 140 mmol), and saturated $CuSO_4$ aqueous solution (2.0 mL) in $CHCl_3$ (10 mL) and MeOH (10 mL) was added dropwise a solution of $NaIO_4$ (6.2 g, 30 mmol) in water (60 mL) at rt for 1 h. After the addition was finished, the organic layer was separated, washed with H_2O, dried over $MgSO_4$, and evaporated. 2'-Adamantylidene-9-benzonorbornenylidene **6** was obtained in quantitative yield (1.61 g). **6**: colorless crystals (from hexane); mp 115—116 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 1.18—1.24 (m, 2H), 1.55—1.97 (m, 14H), 2.56 (br s, 2H), 3.73—3.80 (m, 2H), 7.00—7.08 (m, 2H), 7.10—7.17 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 27.3, 28.4, 28.6, 34.0, 37.3, 38.5, 39.7, 42.8, 119.8, 125.2, 126.9, 141.3, 147.9; IR (KBr) 3070, 3015, 2992, 2968, 2953, 2899, 2862, 2845, 1466, 1446, 755, 730, 675, 572, 467, 457 cm^{-1}. Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.15; H, 8.78.

Hydrogenation of 9 by Ammonium Formate in the presence of Pd/C. Ammonium formate (1030 mg, 16.3 mmol) and 5% palladium on charcol (47 mg) was added to a solution of **9** (447 mg, 1.6 mmol) in $CHCl_3$ (4.0 mL) and MeOH (4.0 mL). After being heated at reflux for 1 day, the insoluble material was removed by filtration on a pad of Celite. The filtrate was washed with H_2O, dried over $MgSO_4$, and evaporated. The compound **6** was obtained in 87% yield (392 mg).

Sulfuration of 6 by Elemental Sulfur in Refluxing *o*-$Cl_2C_6H_4$. A suspension of **6** (970 mg, 3.5 mmol) and elemental sulfur (898 mg, 3.5 mmol as S_8) in *o*-$Cl_2C_6H_4$ (10 mL) was heated under reflux for 48 h. The mixture was evaporated under reduced pressure. The residue was placed on a column of silica gel and the column was eluted with hexane to give 190 mg (20%) of **6** and with $CHCl_3$/hexane (1:4) to give 821 mg (76%) of **14** and 39 mg (4%) of **15**. *anti*-Thiirane **14**: colorless crystals (from CH_2Cl_2 and MeOH); mp 164—166 °C; ^{1}H NMR (400.4 MHz, $CDCl_3$) δ 1.02—1.12 (m, 2H), 1.31—1.40 (m, 2H), 1.40—1.46 (m, 1H), 1.50—1.60 (m, 2H), 1.63 (br s, 2H), 1.70—1.82 (m, 4H), 1.88—1.93 (m, 1H), 1.99—2.04 (m, 2H), 2.23—2.35 (m, 2H), 3.10—3.14 (m, 2H), 7.09—7.15 (m, 2H), 7.16—7.22 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.4, 27.2, 27.6, 36.8, 37.3, 37.4, 38.2, 47.3, 66.1, 79.7, 120.7, 126.1, 146.5; IR (KBr) 3043, 3025, 2983, 2959, 2920, 2903, 2858, 2842, 1451, 1441, 736, 586, 480 cm^{-1}; MS (EI) *m/z* 308 (M^+, 100%), 309 (M^++1, 26%), 310 (M^++2, 8%). Anal. Calcd for $C_{21}H_{24}S$: C, 81.76; H, 7.84. Found: C, 81.72; H, 7.92. *syn*-Thiirane **15**: colorless crystals (from CH_2Cl_2 and MeOH); mp 202—203 °C (decomp.); ^{1}H NMR (400.4 MHz, $CDCl_3$) δ 1.42—1.49 (m, 2H), 1.80—1.90 (m, 6H), 1.93—2.11 (m, 8H), 2.25—2.33 (m, 2H), 3.26—3.32 (m, 2H), 7.09—7.15 (m, 2H), 7.17—7.23 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.8, 27.0, 27.8, 37.2, 37.6, 38.4, 38.8, 49.0, 70.3, 83.0, 120.7, 125.7, 147.6; IR (KBr) 3048, 2998, 2987, 2972, 2918, 2845, 1456, 763, 743, 578, 498 cm^{-1}; MS (EI) *m/z* 308 (M^+, 100%), 309 (M^++1, 26%), 310 (M^++2, 8%). Anal. Calcd for $C_{21}H_{24}S$: C, 81.76; H, 7.84. Found: C, 81.81; H, 7.93.

Sulfuration of 6 by Elemental Sulfur in DMF at 135 °C. A suspension of **6** (8.0 mg, 29 μmol) and elemental sulfur (7.4 mg, 29 μmol as S_8) in DMF (0.6 mL) was heated at 135 °C for 20 h. The mixture was evaporated under reduced pressure to give 15.4 mg of a mixture of **14** (54%), **15** (6%), and **5** (40%).

X-Ray Crystallographic Analysis of *anti*-Thiirane 14. A single crystal of **14** of suitable quality and size was obtained by crystallization from a mixture of CH_2Cl_2 and hexane. Oscillation and nonscreen Weissenberg photographs were collected on the imaging plates of the MAC DIP3000 diffractometer by using Mo-K_α radiation (λ = 0.71073 Å) and the data collection was made by the MAC DENZO program system. Absorption collection was made by multi-scan method (SORTAV). Cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR97 in the maXus program system. The atomic coordinates and the anisotropic thermal parameters of the non-H atoms were refined on F^2 by full matrix least squares using SHELXL-97 {weighting scheme: $w = 1/[\sigma^2(F^2) + (0.0493P)^2]$ where $P = (F_O^2 + 2F_C^2)/3$}. $C_{21}H_{24}S$ (308.49), orthorhombic, space group *Pnma*, $a = 18.295(<1)$, $b = 10.430(<1)$, $c = 8.417(<1)$ Å, $V = 1606.11(10)$ Å^3, $Z = 4$, $Dcalc = 1.276$ Mgm^{-3}, $\mu = 0.196$ mm^{-1}, crystal dimension: 0.23 × 0.19 × 0.14 mm, θ range: 0—27.07°, number of measured reflections: 2020, number of independent reflections: 1844, number of observed reflections: 1423 [$I > 2\sigma(I)$], refined parameters: 159, $R = 0.0499$ [$I > 2\sigma(I)$], $wR_2 = 0.0953$ (all reflections), $S = 0.972$, $(\Delta/\sigma)_{max} = <0.001$, $\Delta\rho max = 0.185$ eÅ^{-3}, $\Delta\rho min = -0.369$ e Å^{-3}.

General Procedure for Sulfuration of 6 by Ph_3CS_XCl. To a solution of **6** in CH_2Cl_2 was added dropwise a solution of Ph_3CS_XCl (1.0 molar equiv.) in CH_2Cl_2 at –78 °C, –18 °C or rt. After being stirred for 2 h at the same temperature, the reaction was quenched by addition of a solution of NaOEt in MeOH. The organic layer was washed with H_2O, dried over K_2CO_3, and evaporated. The residue was placed on a column of silica gel and the column was eluted with $CHCl_3$/hexane (1:4) to give a mixture of **14**, **15**, and **6**.

Sulfuration of 6 by 1.0 molar equiv. of S_2Cl_2 at –78 °C. To a solution of **6** (100 mg, 360 μmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of S_2Cl_2 (49 mg, 360 μmol) in CH_2Cl_2 (5 mL) at –78 °C. After being stirred for 30 min at same temperature, the reaction was quenched by addition of ice water. The organic layer was separated, washed with H_2O, dried over K_2CO_3, and evaporated to give 131 mg of a 68:32 mixture of **14** and **28**. The mixture was placed on a column of silica gel and the column was eluted with $CHCl_3$/hexane (1:4) to give 76 mg of **12** (68%) and with $CHCl_3$ to give 34 mg of **29** (32%). Ketone **29**: colorless crystals (from CH_2Cl_2 and hexane); mp 189—191 °C; ^{1}H NMR (400.4 MHz, $CDCl_3$) δ 0.88 (br s, 1H), 1.28—1.48 (m, 3H), 1.55—1.75 (m, 5H), 1.85 (br s, 1H), 1.91 (br s, 1H), 1.98—2.07 (m, 2H), 2.10—2.22 (m, 2H), 2.26—2.31 (m, 2H), 2.68—2.75 (m, 1H), 3.49—3.52 (m, 1H), 3.87—3.89 (m, 1H), 7.13—7.24 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.3, 23.7, 26.9, 27.5, 31.4, 32.4, 32.8, 32.9, 33.2, 33.3, 39.3, 42.6, 51.5, 54.7, 124.7, 125.0, 126.7, 126.8, 136.3, 142.4, 214.5; IR (KBr) 3036, 2967, 2951, 2905, 2853, 1700, 760, 753, 490 cm^{-1}; MS (FAB) *m*/*z* 293 (MH^+). Anal. Calcd for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 85.97; H, 8.38.

Synthesis of 28 by Reaction of 6 by SO_2Cl_2 at –78 °C. To a solution of **6** (100 mg, 360 μmol) in CH_2Cl_2 (5.0 mL) was added dropwise a solution of SO_2Cl_2 (49 mg, 360 μmol) in CH_2Cl_2 (3.0 mL) at –78 °C. After being stirred for 15 h at the same temperature, the reaction was quenched by addition of ice water. The organic layer was separated, washed with H_2O, dried over K_2CO_3, and evaporated to give 125 mg of **28** (quantitatively). The ^{1}H and ^{13}C NMR spectra of **28** are consistent with those of the product by the reaction of **6** with S_2Cl_2. *vic*-Dichloride **28**: colorless crystals (from CH_2Cl_2 and MeOH); mp

126—127 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C) δ 1.02—2.65 (m, 18H), 4.76—4.14 (br s, 2H), 6.98—7.22 (m, 4H); ^{1}H NMR (400.4 MHz, $CDCl_3$, –50 °C) δ 0.43—0.44 (m, 1H), 1.01—1.07 (m, 1H), 1.19—1.23 (m, 2H), 1.30—1.36 (m, 1H), 1.52—1.66 (m, 4H), 1.77—1.81 (m, 2H), 1.98—2.02 (m, 1H), 2.16—2.23 (m, 2H), 2.41—2.47 (m, 2H), 2.56—2.61 (m, 1H), 2.98—2.99 (m, 1H), 3.80—3.87 (m, 1H), 4.14—4.16 (m, 1H), 7.14—7.20 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, –50 °C) δ 25.5, 26.0, 27.0, 29.1, 33.5, 35.9, 36.0, 36.1, 38.0, 38.1, 40.3, 55.4, 57.3, 89.2, 97.8, 120.2, 121.6, 126.2, 126.6, 143.2, 144.2; IR (KBr) 3032, 3006, 2976, 2953, 2901, 2862, 1470, 1453, 1279, 1099, 862, 797, 763, 746, 582, 508 cm^{-1}; MS (EI) *m/z* 129 (100%), 346 (M^+, 94%), 348 (M^++2, 61%), 350 (M^++4, 12%). Anal. Calcd for $C_{21}H_{24}Cl_2$: C, 72.62; H, 6.97. Found: C, 72.57; H, 7.01.

General Procerdure for Sulfuration of 6 by S_XCl_2 at –78 °C. To a solution of **6** (100 mg, 360 μmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of S_XCl_2 (1.0 or 0.5 molar equiv.) in CH_2Cl_2 (5.0 mL) at –78 °C. After being stirred for 30 min at the same temperature, the reaction was quenched by addition of ice water. The organic layer was separated, washed with H_2O, dried over K_2CO_3, and evaporated. A ratio of the the products was estimated by ^{1}H NMR.

General Procerdure for Reactions of 14 or 15 with 1.0 molar equiv. of S_XCl_2 at –78 °C. To a solution of **14** or **15** in CH_2Cl_2 was added dropwise a solution of S_XCl_2 (1.0 molar equiv.) in CH_2Cl_2 at –78 °C. After being stirred for 30 min at the same temperature, the reaction was quenched by addition of ice water. The organic layer was separated, washed with H_2O, dried over K_2CO_3, and evaporated. A ratio of the the products was estimated by ^{1}H NMR.

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REFERENCES AND NOTES

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